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A METHOD OF PRODUCING CONDUCTIVE POLYMER COMPOSITES
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SPECIFICATION /225*

1. Title of the Invention:

A Method of Producing Conductive Polymer Composites

2. Claims:

(1) A method of producing composites of polythiophenes and electrolytes which is characterized by the fact that an electrolytic oxidative polymerization of thiophene monomers is carried out in a solution containing a polymer electrolyte having an anion group in which at least the α-position is substituted with a fluorine atom.

3. Detailed Description of the Invention

[Industrial Field of Application]

This invention pertains to a method of producing conductive polymer composites. More precisely, this invention pertains to a method of producing composites of polythiophenes and electrolytes, using an anion group of the electrolyte as a fixed dopant.

Conductive polymers are currently noted as new conductive materials such as conductors, semiconductors, batteries, display elements, photoelectric conversion elements and sensors, based on new physical properties and electrochemical characteristics.

*Numbers in the margin indicate pagination in the foreign text.

[Prior Art]

Since the time when the conductivity of polyacetylene was found to be significantly improved by ion doping methods, a variety of kinds of ion doping type conductive polymers have been proposed.

Dopants for P-type conductive polymers include macro cyclic molecules and polymer electrolytes as well as smaller halogen ions. Doping methods for various dopants, features of the conductive polymers and development of applications are investigated as new technologies for the purpose of developing functioning of conductive polymers.

As an example of the above-mentioned dopants, inorganic anions are applicable. Although dopants can be doped in large quantities in conductive polymers, the problem is that dopants are not evenly doped. For this reason, the polymers are not satisfactory in terms of conductivity. In addition, the drawback of these polymers is that they are brittle and demonstrate poor self-sufficiency.

For this reason, recently polymer electrolytes having anion /226 groups are proposed as dopants. For example, in the Kokai Patent No. Sho 59-98165, conductive polymer compositions using polymers as dopants were disclosed. These compositions contain polymer doping agents such as sulfonated polyethylenes, sulfonated polystyrenes, sulfonated poly(2,5-dimethylphenylene oxide),

sulfonated polyvinylalcohols, and sulfonated styrene/(hydrogenated)butadiene copolymers. The anion groups are made of sulfonate groups. This proposal demonstrated that the conductive polymer composites obtained are more stable and self-contained compared to the conventional conductive polymers using inorganic anions as dopants. However, they are not always satisfactory as conductive materials in terms of chemical and physical stabilities. On the other hand, the problem is in that the doping rate which is the important factor of ion dopant type conductive polymers is much lower than that in the case when using common inorganic anionic dopants since the concentration of the conductive polymer is higher on one side and the polymer electrolyte concentration is higher on the other side. According to our investigation, the sulfonate groups of the sulfonated polymer doping agents are easily dissociated in an aqueous solution, while they are not easily dissociated in a non-aqueous solution. This is a big barrier against practical operations.

Uses of fluorine-containing polymer electrolytes as polymer dopants are also proposed due to excellent chemical stability compared to the above-mentioned sulfonated polymers. For example, when using a cell in which a monomer solution forming a conductive polymer and an oxidant solution are separated using a fluorine-containing polymer electrolyte as a diaphragm, the conductive polymer is chemically polymerized from the surface at

the side of the oxidant for fluorine-containing polymer electrolytes in order to synthesize composites of conductive polymers and fluorine-containing polymer electrolytes. However, even in this method, the doping rate of the polymer electrolytes is not satisfactory. The problem is in that the dopant is unevenly doped on the film. In the composites of conductive polymers and polymer electrolytes which are synthesized by chemical polymerization, anion groups of the polymer electrolytes and anions introduced by oxidative polymerization are introduced as dopants. As a result, a composite film of conductive polymers and polymer electrolytes is formed with composite dopants consisting of fixed dopants and movable dopants.

In the Kokai Patent No. Sho 63-98972, the composites of conductive polymers and fluorine-containing polymer electrolytes are used as positive pole active substances in the secondary batteries. According to this proposal, when the composite is used as a battery positive pole, the self discharge rate of the positive pole is reduced so that durability of the batteries is improved. In particular, a composite powder of fluorine-containing polymer electrolytes and the conductive polymers was prepared by the chemical polymerization method. However, the doping rate of the polymer electrolyte of the composites obtained by this method was very low. In an operational example, a fluorine-containing polymer electrolyte is doped only at 25% in

polyaniline. Although all the anion groups of the fluorine-containing polymer electrolyte are doped, the doping rate is only 3% per unit polyaniline. Since the discharge capacity of the composites is very high, the anions introduced from ammonium persulfate as an oxidant are assumed to be major dopants compared to the fluorine-containing polymer electrolyte anion groups. Therefore, these composites are not satisfactory in terms of stability and self-sufficiency.

As described above, in the electrolytes having anion groups as was proposed conventionally, namely in the composites consisting of polymer electrolytes and conductive polymers, the doping rate of the polymer electrolytes is much lower than the dopant rate reported for inorganic anions. Since large amounts of both anion groups of polymer electrolytes and other anionic groups are frequently doped, the composites obtained are assumed to be composite dopants consisting of fixed dopants and movable dopants. In addition, the film obtained does not always have a uniform composition and physical and chemical stability are not sufficient. The problem is in that the composites do not function well in various solvents.

[Problems that this Invention Intends to Solve] /227

The purpose of this invention is to provide fixed dopant type conductive polymers demonstrating a high doping rate. This invention proposes a method of producing composites consisting of

conductive polymers and electrolytes having anion groups in which only anion groups of the electrolytes are used as dopants and are doped at a high doping rate as high as that of the inorganic halogen anions, and also are fixed in the conductive polymers. The composites function as so-called fixed dopants, demonstrate uniform compositions with excellent physical and chemical stabilities, and can function in a variety of kinds of solvents.

[Means to Solve the Problems]

The inventors earnestly investigated the above-mentioned subjects of concern and found the fact that fixed dopant type conductive polymers demonstrating a high doping rate can be obtained by producing polymers by the electrolytic oxidative polymerization. This finding led us to achieve this invention. This invention pertains to a method of producing composites of polythiophenes and electrolytes which is characterized by the fact that an electrolytic oxidative polymerization of thiophene monomers is carried out in a solution containing a polymer electrolyte having an anion group in which at least the α-position is substituted with a fluorine atom.

This invention will be explained in detail below.

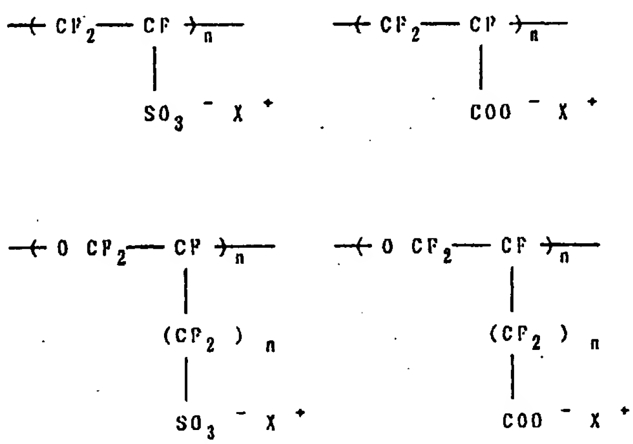
Figure 1 shows a redox model for the fixed dopant type conductive polymers in this invention. In the common movable dopant type conductive polymers using inorganic anions as dopants, anions as dopants move around through the conductive

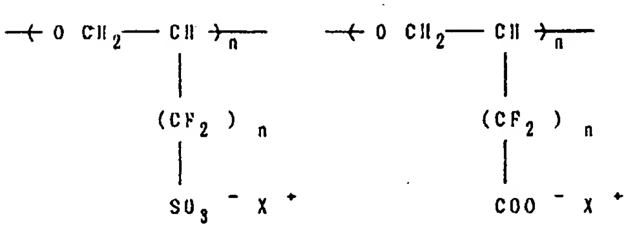
polymer as the oxidative/reductive reactions proceed as shown in Fig. 2. On the other hand, in the fixed dopant type conductive polymers, dopants are fixed in the conductive polymer as shown in Fig. 1 so that dopants cannot move around through the conductive polymers as the oxidative/reduction reactions progress. For this reason, in this fixed dopant type conductive polymer, pair ions of the anions fixed in the conductive polymer, namely cations, move around through the conductive polymer along with the oxidative/reductive reactions. As explained above, the fixed dopant type conductive polymer demonstrates a redox mechanism which is clearly different from that of the movable dopant type conductive polymer.

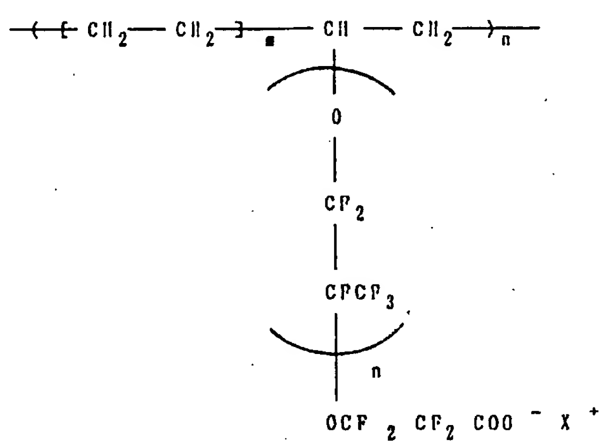
The polymer electrolytes having anion groups in which at least the α-position is substituted with a fluorine atom in this invention's method of producing conductive polymer composites do not dissociate anion groups into a solvent and are desirable as anion-containing electrolytes with a molecular size of oligomers to polymers. When forming composites with conductive polymers using such electrolytes, dopant anions (electrolytes having anion groups) become fixed dopants which do not move around through the conductive polymer along with the progress in oxidative/reductive reactions. In addition, at least the α-position in the electrolyte is substituted with a fluorine atom so that the conductive polymer compositions obtained can function not only in

an aqueous solution, but also in a variety of type of solvents including non-aqueous solutions. The reason for this is not clearly known. It seems that the electrolyte used in this invention can dissociate anion groups due to electron receptability of the fluorine even in a non-aqueous solution.

Actual examples of the above-mentioned electrolytes include oligomers or polymers with the following structures:







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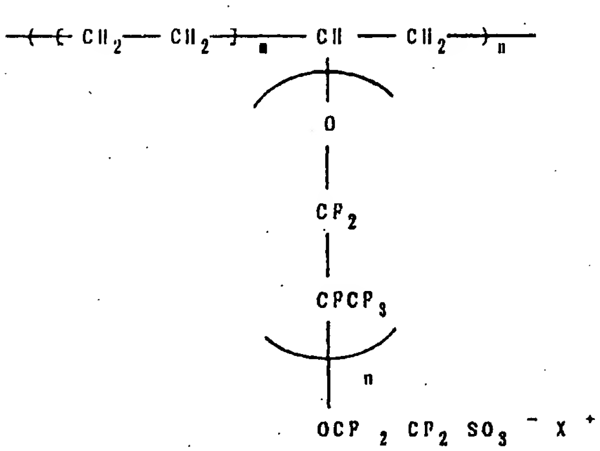
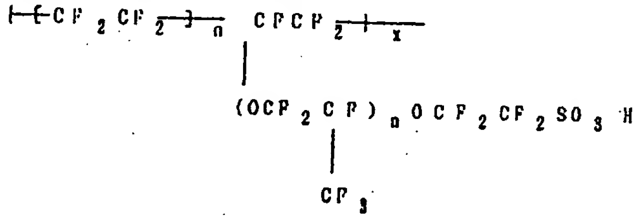


More concretely, polymer electrolytes include copolymers of tetrafluoroethylene with perfluoro-3,6-dioxa-methyl-7-octensulfamate having the following structures:



The solutions used for the electrolytic oxidative polymerization can be obtained by dissolving the aforementioned electrolytes in a soluble solvent. The following polar solvents including alcohols, ketones, organic acids, aldehydes, and esters are available as soluble solvents. The concentration of the solution is not particularly specified. However, it is desirable that the concentration of the electrolyte be 10^{-3}mol/dm^3 or greater.

Thiophenes used in this invention include thiophene and thiophene derivatives. In particular, considering the structure of the conductive polymers, the substituents are preferably present at the 3- and/or 4-positions in the derivatives. Such derivatives are 3-methylthiophene and 3-methoxythiophene.

The electrolytic oxidative polymerization is carried out by an anodic reaction. As an anode, metals such as platinum, conductive glass prepared by coating a conductive substance such as ITO on the surface and glassy carbon can be selected from arbitrary conductive substrates.

As electrolytic oxidative polymerization conditions, constant current electrolytic methods, constant voltage electrolytic methods, pulse electrolytic methods, and voltage scanning electrolytic methods are available.

For example, in the case of a constant current electrolytic method using an electrolyte solution containing thiophenes, the electrolytic oxidative polymerization is carried out at a constant current: $10^{-2}mA/cm^2$ to $10^1mA/cm^2$ to obtain a conductive polymer composite. In the case of a constant voltage electrolytic method using an electrolyte solution containing thiophenes, a voltage which is greater than the oxidative voltage of thiophenes such as +1.5 to +2.5V vs SCE is applied to an anode to carry out an electrolytic oxidative polymerization and a conductive polymer composite is obtained.

The solution temperature when carrying out the electrolytic oxidative polymerization can be appropriately adjusted based on the properties of the conductive polymer composites to be prepared. In order to obtain conductive polymer composites with a high doping rate, physical and chemical stability and uniform composition stability, it is desirable to maintain the solution temperature at room temperature or below.

The conductive polymer composites obtained above are fixed dopant type composites using only anion groups of electrolytes as dopants and the doping rate of the dopants ranges from 0.15 to

0.3 per one unit of polythiophenes. This doping rate of the anions is as high as that of inorganic halogen anions. In addition, the conductive polymer composites obtained demonstrate excellent physical and chemical stability in an uniform composition and function well even in various solvents.

The movable ions in the fixed dopant type conductive polymer composites as produced by this invention's method are cations which are pair ions of the fixed anions so that the application to electrochemical elements is desirable. For example, desirable characteristics as positive pole of the secondary batteries are presented. For example, if it is used as a positive pole of a lithium battery, the movable species are same at the positive pole and negative pole so that batteries with little changes in the electrolyte concentration can be formed. /229

[Examples]

This invention will be explained in detail in the following Examples. However, this invention will not be limited to these examples.

Example 1, Comparison Example 1

Using platinum plate (effective electrode area 0.5 cm^2) as an anode and an alcohol solution (electrode 5 wt %, water 10 wt %) of an electrolyte (a product by DuPont, Naphyon) containing a copolymer of tetrafluoroethylene and perfluoro-3,6-dioxa-methyl-

As a Comparison Example 1, an anodic oxidative polymerization was carried out using an acetonitrile solution containing 0.1mol/dm^3 tetraethylammonium perchlorate containing 0.01mol/dm^3 of thiophene at a constant current of 0.5mA/cm^2 to 0.6 C/cm^2. As a result, a polythiophene homopolymer containing ClO_4^- ions of tetraethyl ammonium perchlorate as a dopant was obtained. The polythiophene homopolymer was brittle and unstable. Using this polythiophene homopolymer as a test electrode, cyclic voltammetry was carried out under the same conditions as in Example 1. The results are indicated by broken lines in Figs. 3 and 4. As shown in Fig. 4, no redox was found in an aqueous sodium polystyrenesulfonate solution. In the case of a homopolymer, an anion transfer redox accompanying anion movement along the oxidative/reductive reactions was found. However, if macro polystyrenesulfonate anions are formed, anion transfer is disabled. In contrast, as clearly shown in Figs. 3 and 4, the conductive polymer composite indicated the almost identical reversible voltamogram regardless of the sizes of the anion species. As a result, the conductive polymer composite was found to demonstrate a cation transfer redox.

Moreover, the transfer ions involved in oxidative/reductive reactions of the conductive polymer composite were identified by EFMA analysis. The results are shown in Fig. 5-a. The analytical data for the homopolymer obtained in Comparison

Example 2

A conductive polymer composite was prepared and evaluated as in Example 1 except that 3-methylthiophene was used instead of thiophene. The conductive polymer composite obtained above was found to be a physically/chemically stable self-contained uniform composite film in which the doping rate was 0.25. It was identified as a cation transfer type redox based on the electrochemical evaluation. The redox capacity was 95% in propylene carbonate containing 1mol/dm^3 lithium perchlorate.

Comparison Example 2

An anodic oxidative polymerization was carried out using a platinum plate (effective electrode area: 0.5cm^2) as an anode and an aqueous solution containing 0.1mol/dm^3 of thiophene and 20g of potassium polystyrenesulfonate as an electrolytic solution, at a constant current of 0.5mA/cm^2 to 0.6 C/cm^2 to obtain a conductive polymer composite consisting of polythiophene and polystyrene sulfonaic acid.

A cyclic voltammetry was carried out in propylene carbonate containing 1.0mol/dm^3 of lithium perchlorate using the conductive polymer composite as a test electrode and platinum plate as a facing electrode and a saturated calomel electrode as a reference electrode. The capacity was 5% of the redox capacity estimated from the polymerization electrical capacity. It was assumed that a sufficient capacity was not achieved due to difficulty in the

as high as that of inorganic halogen anions, have a uniform composition which is physically/chemically stable and can function well even in various kinds of solvents.

The composites obtained present new fixed dopant type functions (cation transfer type). Therefore, these composites are highly noted in the field of applications of a variety of kinds of conductive polymers.

4. Brief Explanation of the Figures /231

Figure 1 is a diagram showing a redox model of the fixed dopant type conductive polymer obtained in this invention.

Figure 2 is a diagram showing a redox model of the movable dopant type conductive polymers.

Figure 3 is a diagram showing cyclic voltamograms in an aqueous potassium chloride solution of the conductive polymer composites and the conductive polymers obtained in Example 1 and Comparison Example 1.

Figure 4 is a diagram showing cyclic voltamograms in an aqueous sodium polystyrenesulfonate solution of the conductive polymer composites and the conductive polymers obtained in Example 1 and Comparison Example 1.

Figure 5 is a diagram showing the results of EFMA analysis for the conductive polymer composites and the conductive polymers obtained in Example 1 and Comparison Example 1.

Figure 1
Key: A) Polythiophene; B) Fixed electrolyte; C) Bulk solution; D) Oxidation; E) Polythiophene; F) Fixed electrolyte; G) Bulk solution; H) Reduction.

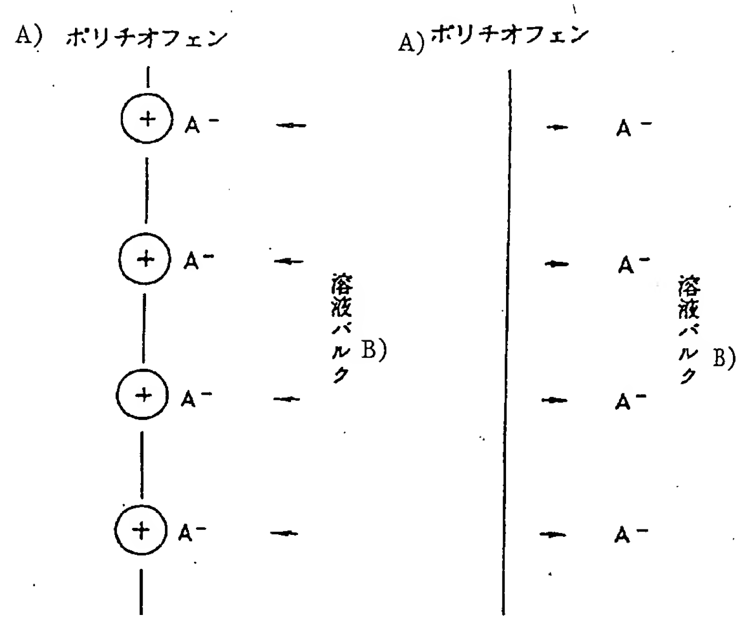
Figure 2
Key: A) Polythiophene; B) Bulk solution.

Figure 3
Key: A) Current density; B) Polythiophene composite; C) Polythiophene

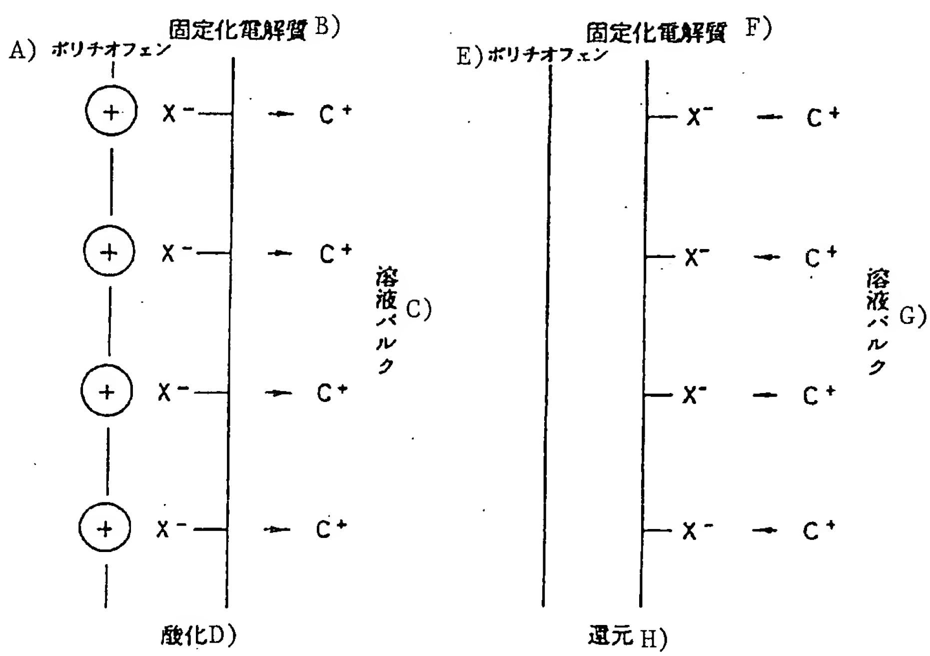
Figure 4
Key: A) Current density; B) Polythiophene composite; C) Polythiophene

Figure 5
Key: A) Intensity; B) Reduction; C) Oxidation; D) X-ray energy/KeV.

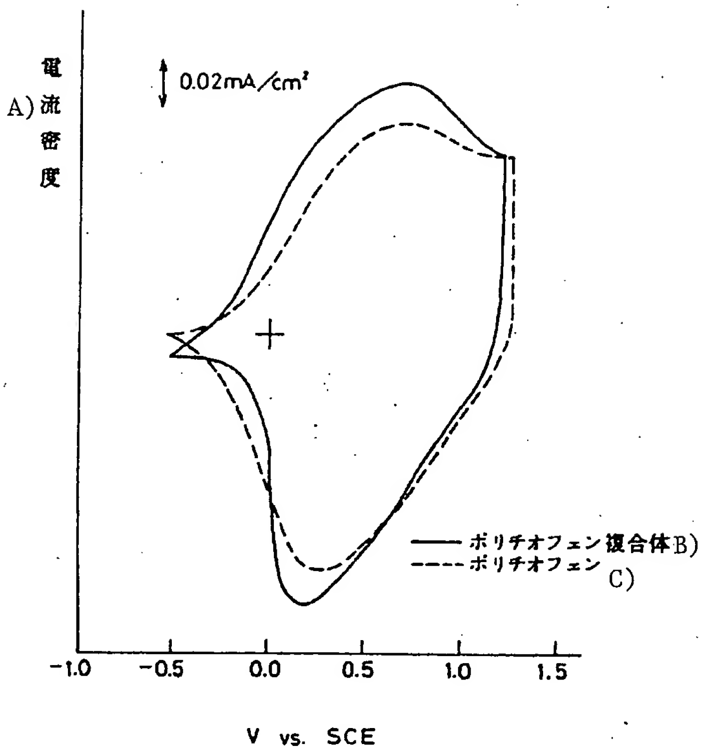
[Figure 2] 第2図



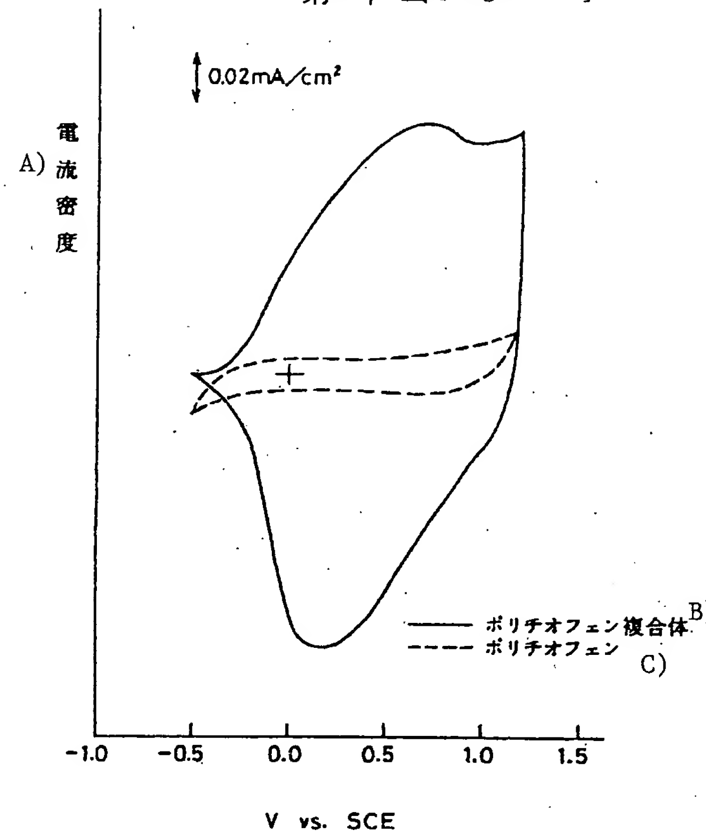
第1図 [Figure 1]



第 3 図 [Figure 3]



第 4 図 [Figure 4]



第 5 図 [Figure 5]